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(54) Composition for the production of artificial marble or granite.

(57) Described is a composition for the production of artificial marble or granite, with excellent aesthetic properties and patterns and tonalities which cannot be found in natural materials, containing a polymerizable poly(allyl carbonate) of a polyol and a mineral filler. The mineral filler is of the carbonate type in the case of marble, and of the silicate or silica type in the case of granite, and is in the form of particles of which 40 to 100% by weight have a particles size of at least 0.5 mm.

A process for the production of artificial marble and granite is also described. The artificial marble and granite so produced requires a limited quantity of polymerizable poly(allyl carbonate) binder, has excellent aesthetic properties and high aging resistance, making it suitable for outside use.

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The present invention relates to a composition for the production of artificial marble or granite. The invention also relates to a process for transforming this composition into artificial marble or granite and to the artificial marble and granite thus obtained.

Artificial marble and granite in block or panel form, generally composed of a mineral filler dispersed in a polymer matrix, is already known in the art, and is described, for example, in US-A-4,698,010, DE-A-20 54 168 and Italian patent 10563/88. A polyester resin or a polymethyl methacrylate are generally used for this purpose, mixed with the inorganic filler, and subjected to hardening after a compaction treatment. Unfortunately, when a polyester resin is used, the product cannot be used outside because of its limited aging resistance, especially when exposed to UV radiation, whereas when a polymethyl methacrylate is used, the disadvantages basically consist in the use of a volatile and toxic polymerizable monomer.

Artificial marble composed of the product of the polymerization of a poly(allyl carbonate) has also been described in the art. In particular, in JP-A-61-111953 an artificial marble composed of the polymerization product of a poly(allyl carbonate) of a polyol which contains fine silica or hydrated alumina as mineral filler is described. In particular, the particle size of the mineral filler ranges from 1 to 30 µm preferably from 5 to 20 µm. JP-A-63-237989 describes a composition for the production of artificial marble composed of a bis-(allyl carbonate) containing an oligomer of a di- or tri-functional alcohol and an inorganic filler. In particular, the inorganic filler is in the form of particles having a size of from 1 to 30 µm preferably of from 5 to 10 µm. JP-A-63-246660 describes an artificial marble including a resinous binder and a balloon-shaped inorganic filler, where the inorganic filler is in the form of particles of 10 to 100 µm in size. Finally, IT-A-19814 A/90 describes an artificial marble with improved colouring and scratch resistance, composed of the polymerization product of a poly(allyl carbonate) of a polyol containing cristobalite as mineral filler. In particular, the particle size of the mineral filler ranges from 1 to 200 µm, preferably from 2 to 50 µm. This artificial marble with poly(allyl carbonate) binder has an improved aging resistance. However, high quantities of organic binder are required, making the process costly and consequently hindering the commercial development of the product.

It has now been found that by using a gross mineral filler of the carbonate type (in the case of marble) or of the silicate or silica type (in the case of granite), combined with a polymerizable bis(allyl carbonate), compositions may be obtained which can easily be transformed into marble and granite with excellent aesthetic properties, requiring only a reduced quantity of organic binder.

Accordingly, this invention provides a composition for producing artificial marble or granite, containing a liquid and polymerizable polyol-based poly(allyl carbonate) binder (a) and a mineral filler (b), wherein:

- the mineral filler (b) is of the carbonate type in the case of marble, and of the silicate or silica type in the case of granite,
- the carbonate, silicate or silica mineral filler is in the form of particles of which 40 to 100% by weight have a particle size of at least 0.5 mm;
- the polymerizable poly(allyl carbonate) binder (a) is present in quantities of from 4 to 30 parts by weight per 100 parts by weight of the combined weight of poly(allyl carbonate) (a) and mineral filler (b).

In accordance with a preferred embodiment, 50 to 80% by weight of the mineral filler are composed of particles of at least 0.5 mm in size, the remainder being composed of particles of less than 0.5 mm in size, preferably particles having a size ranging from 1 to 499 µm. These smaller particles may be of the same kind or different from the larger particles. The maximum size of the larger particles is not of critical importance and can reach values of 10 - 20 cm as, for example, in the production of artificial breccia marble. However, in the preferred embodiment the particle size of the larger filler particles does not exceed 20 mm.

Preferably, the polymerizable poly(allyl carbonate) is present in the composition in quantities of from 6 to 20 parts by weight per 100 parts by weight of the combined amount of said poly(allyl carbonate) and said mineral filler. Especially satisfactory results may be obtained by using quantitites of as little as 7 to 8 parts by weight of polymerizable poly(allyl carbonate) per 100 parts by weight of the sum of said poly(allyl carbonate) and said mineral filler.

Useful fillers for the purpose of this invention are carbonate, silicate or silica mineral fillers. Examples of these are natural marble, granite and silica sand. The finer mineral filler particles may also be composed of finely ground natural marble, granite or silica sand and/or other materials such as hydrated alumina, talc, silicas, graphite, mica or mixtures thereof.

The finer mineral filler particles may partially be substituted (usually in amounts up to 50% by weight) by long and/or short glass fibres. These fine mineral fillers and glass fibres have the function of filling the interstices between the gross fillers in the final conglomerate, and of consequently giving compaction and mechanical resistance to the resulting material at the end of the production process. Some fillers also have

a special function, as in the case of hydrated alumina which, as is well-known, renders the material in which it is contained flame resistant.

In particular, it has been found that the higher the particle size of the gross mineral filler, especially in the case of artificial granite, the more will the resulting material resemble ordinary granite at the end of the process.

Both fine and gross mineral fillers can be pre-treated with compatibilizing agents of the silane type, such as gammamethacryloxypropyl triethoxysilane, vinyl triethoxysilane and trimethylsilane. These compatibilizing agents have the effect of closely binding the organic matrix to the mineral filler, creating a more compact and continuous structure in the artificial marble and granite, with a consequent further improvement in mechanical characteristics thereof.

The polymerizable polyol-based poly(allyl carbonate) binder which is suitable for the purposes of this invention, is generally composed of at least one poly(allyl carbonate) of a polyol containing from 2 to 6 hydroxy groups in the molecule, in the form of a monomer and/or oligomer.

Poly(allyl carbonates) of polyols suitable for the purposes of this invention can, for example, be selected from:

- bis(allyl carbonates) of (preferably C_2-C_{12}) diols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, pentanediol, hexanediol, di-(hydroxymethyl)-cyclohexane, neopentyl glycol and di(hydroxymethyl)-tricyclodecane;
- tris(allyl carbonates) of (preferably C_3-C_{15}) triols such as glycerol, trimethylolpropane and tris-(hydroxyethyl)isocyanurate;
- tetra(allyl carbonate) of pentaerythritol;
- hexa(allyl carbonate) of dipentaerythritol.

Mixed poly(allyl carbonates), containing radicals of two or more different polyols in the same molecule, may also be used.

In one of the preferred embodiments, the poly(allyl carbonate) of the polyol is bis(allyl carbonate) of diethylene glycol monomer of general formula (I):

$$CH_2{=}CH{-}CH_2{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}(R{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O)_n{-}CH_2{-}CH{=}CH_2 \qquad (I)$$

where R is the diethylene glycol radical and n = 1.

Compound (I) can be prepared by reacting diethylene glycol bis(chloroformate) with allyl alcohol as described, for example, in "Encyclopedia of Chemical Technology", Kirk-Othmer, III Ed., Vol. 2, pages 111 - 112.

According to another preferred embodiment, the poly(allyl carbonate) of the polyol is a mixture of bis-(allyl carbonate) of diethylene glycol monomer [n = 1 in formula (I)] with one or more oligomers of bis(allyl carbonate) of diethylene glycol [n = 2 to 10 in formula (I)]. Monomer/oligomer mixtures containing from 20 to 90% by weight of monomer can be used to particular advantage.

These mixtures can be prepared simply and conveniently by means of a transesterification reaction between diallyl carbonate and diethylene glycol, operating in the presence of a basic catalyst, as described, for example, in EP-A-35304.

In another preferred embodiment, the poly(allyl carbonate) of the polyol is a mixture of:

- bis(allyl carbonate) of diethylene glycol monomer;
- bis(allyl carbonate) of diethylene glycol oligomer (as defined above); and
- tris(allyl carbonate) of tris(hydroxyethyl)isocyanurate.

This mixture will preferably contain from 10 to 50% of the first component; from 20 to 70% of the second component; and from 5 to 60% by weight of the third component. The third component may be partially oligomeric (for example up to 50% by weight).

Polymerizable mixtures of the above composition are described, for example, in US-A-4,812,545.

In accordance with another preferred embodiment, the poly(allyl carbonate) of the polyol is the product of the transesterification of a mixtur of diallyl carbonate, diethylene glycol and tris(hydroxyethyl)-isocyanurate as described, for example, in EP-A-302 537.

In another preferred embodiment th poly(allyl carbonate) of th polyol is a mixture of:

- bis(allyl carbonate) of diethylene glycol monomer;
- bis(allyl carbonate) of diethylene glycol oligomer (as defined above); and
- tetra(allyl carbonate) of pentaerythritol.

This mixture will preferably contain from 10 to 50% of the first component; from 20 to 70% of th second component; and from 5 to 60% by weight of the third component. The third component may b partially oligomeric.

According to another preferred embodiment, the poly(allyl carbonate) of the polyol is obtained by the transesterification of a mixture of diallyl carbonate, ethylene glycol and pentaerythritol as described, for example, in EP-A-302 537.

In accordance with another preferred embodiment, the polyol-based poly(allyl carbonate) may be partially substituted (up to a maximum of 40% by weight) by a monofunctional vinyl and/or (meth)acrylic monomer, such as vinyl acetate, vinyl versatate and methyl methacrylate.

In another preferred embodiment the poly(allyl carbonate) of the polyol is a mixture of:

- bis(allyl carbonate) of neopentyl glycol monomer;
- bis(allyl carbonate) of neopentyl glycol oligomer, defined in the same way as the diethylene glycol oligomer; and
- tris(allyl carbonate) of tris(hydroxyethyl)-isocyanurate.

The above mixture will preferably contain from 10 to 70% of the first component; from 20 to 70% of the second component; and from 5 to 60% by weight of the third component.

The third component may be partially oligomeric.

In accordance with another preferred embodiment, the poly(allyl carbonate) of the polyol is obtained by means of the transesterification of a mixture of di(allyl carbonate), neopentyglycol and tris(hydroxyethyl)-isocyanurate.

The composition for producing artificial marble or granite of the present invention may contain, in addition, a polymerization initiator for the poly(allyl carbonate) (a) which is normally selected from peroxides and azo-compounds. For this purpose, it is preferable to use a percarbonate, especially dicyclohexyl peroxy-dicarbonate or diisopropyl peroxy-dicarbonate. The quantity of initiator usually ranges from 1 to 10% by weight, and preferably from 3 to 7% by weight, with respect to the weight of the polyol-based poly(allyl carbonate) (a).

The composition for producing artificial marble or granite of this invention may also contain, additionally, limited quantities of one or more silanes as a substitute of or in addition to those which may be deposited on the mineral filler. Other additives which may be incorporated in ths mixture (preferably in limited quantities) are: dispersers and/or wetting agents for the mineral fillers, deaerating agents, viscosity reducing agents, antisettling agents, internal release agents (especially of the silicone type) to facilitate the detachment of the product from the mould, titanium dioxide and organic or (preferably) inorganic coloured dyes, organic and/or inorganic flame retarding agents, metallic dyes and/or flakes, organic or inorganic pearly dyes and/or flakes, stabilizers in general, such as UV absorbers of the hydroxy-benzophenone and benzotriazole type and/or UV stabilizers such as sterically hindered amines (HALS).

The UV absorbers are preferably hydroxybenzophenones such as:

- CHIMASSORB® 90 (CIBA): 2-hydroxy-4-methoxybenzophenone
- CHIMASSORB® 81 (CIBA): 2-hydroxy-4-octoxybenzophenone.

The HALS-type UV stabilizers are agents which scavenge the initial promoter radicals of the radicalic decomposition of the polymer, and are preferably derivatives in the 4-position of 2,2,6,6-tetramethylpiperidine.

The amino group of the piperidine ring may be of the secondary or tertiary type (substituted by methyl, for example).

These HALS stabilizers, moreover, may be non-reactive additives in the monomeric mixture, or they may be reactive and be chemically inserted into the polymeric chain during the polymerization of the mixture.

Some non-limiting examples of these HALS stabilizers are:

- TINUVIN® 770 (CIBA)
  [bis(2,2,6,6-tetramethyl-4-piperidyl)-sebacate]
- TINUVIN® 292 (CIBA)
  [bis(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacate]
- UVASIL® 299 (ENICHEM SYNTHESIS)
  [poly-methylpropyl-3-oxy-[4-(2,2,6,6-tetramethyl)-piperidinyl]siloxane]
- 2,2,6,6-tetramethyl-4-piperidyl-acrylate.

Both the hydroxybenzophenone and the HALS derivatives may be added individually and as alternatives, respectively, in quantities of, e.g., from 0.01 to 2%, and preferably from 0.1 to 1.5% by weight with respect to the catalyzed monomeric mixture; or both types of products may be used together in a total quantitiy of, e.g., from 0.02 to 3%, and preferably from 0.2 to 2% by weight with respect to the catalyzed

monomeric mixture.

The second case is preferable in that both products together produce a synergic stabilizing effect.

Another aspect of the present inv ntion relates to a process for the preparation of artificial marble or granite, comprising the steps of:

(a) preparation of one of the above compositions for producing artificial marble or granite by mixing the components therof;

(b) pouring the resulting composition into a mould and compacting it, optionally under vacuum to eliminate any occluded air;

(c) polymerization of the polymerizable organic matrix, by means of a suitable thermal cycle, to obtain a slab or block; and

(d) finishing the slab or block thus obtained.

In particular, step (a) can be carried out in a normal planetary mixer for heterogeneous mixtures in the open air. In step (b) the mould can be treated with a release agent, preferably of the silicone type, or protected with a sheet of polyethylene, polyvinylchloride or any other suitable material. The mould will have the shape of a flat slab or parallelepiped block, and can be subjected to vacuum to allow the evacuation of interstitial air during or after compaction. The latter may be carried out by shaking or vibration. Step (c) can be carried out directly inside or also outside the mould, when the moist panel covered with the protective sheet has become self-consistent and can be extracted from the mould. Suitable thermal cycles for the polymerization of the poly(allyl carbonate) of the polyol can be at a temperature ranging from about 40 to about 100 °C (for example 1 hour at 60 °C, 1.5 hours at 70 °C and 1 hour at 80 °C) or isothermal at about 50 to 60 °C (for example 8 hours at 60 °C). During polymerization, the surfaces of the block or panel should not be in contact with the air to prevent the inhibiting effect of oxygen on the radicalic polymerization. Finally, step (d) may include operations such as the cutting and sizing of the slabs or blocks and their polishing. In particular, in the case of artificial granite, the cutting can be carried out with diamond-pointed tools, and the polishing with abrasive elements based on silicon or boron carbide.

The process described above is particularly advantageous when low quantities of polymerizable poly-(allyl carbonate) of a polyol are used, in particular quantities of less than 10% by weight, i.e., amounts just sufficient to wet the mineral filler. In particular, the compaction in step (b), which can be carried out by using the known techniques, e.g. operating under vacuum and with vibro-compression for short periods of time (for example 60 seconds), allows the extraction of a slightly wet and self-consistent slab with a plastic consistency, which can easily be handled before the polymerization of the poly(allyl carbonate) of the polyol.

The artificial marble and granite of the present invention has excellent aesthetic properties, with patterns and chromatic tonalities which cannot be found in natural materials, and has various advantages with respect to products already known in the art. In particular, compared to similar marble and granite based on polyester resins, it has:

- a better aesthetic appearance of the polished surfaces; these surfaces are in fact shining and not yellowish and show a smaller "orange-peel" effect,
- a better thermal resistance, particularly to cigarette burns,
- a better resistance to chemical agents, solvents and staining in general, and
- a much better external aging-resistance, especially with respect to UV radiation.

Even if this improved aging-resistance of the marble and granite of the present invention compared to those based on polyester resins, is already quite evident when the respective formulations do not contain light stabilizers, it becomes even more apparent when hydroxybenzophenones and/or HALS UV light stablizers, e.g. those described above, are present.

An experiment was carried out by exposing test samples having a flat, smooth surface, to accelerated aging in the following two apparatus:

- ATLAS Ci 65 Weather-O-Meter;
  . 6500 Watt Xenon lamp;
  . Relative humidity 50%;
  . Temperature of the black panel: 60 °C;
  . Exposure cycle: continuous irradiation;
  . Exposure time: 2000 hours.
- UV-CON ATLAS:
  . FS 40 fluorescent lamp;
  . Exposure cycle: irradiation for 8 hours at 60 °C, then darkness for 4 hours, at 40 °C, with abundant condensed moisture on the surface of the sample;
  . Exposure time: 1000 hours.

Exposure in the second apparatus is more drastic compared to that in the first one.

The evaluation consisted in the measurement of the difference in colour of the samples from the beginning to the end of exposure; th valuation parameters were deduced from the tristimulus colorimetry, and in particular the following values were determined:

- Δ E*: total variation in colour
- ΔC*: variation in colour excluding the variation in lightness.

The following conclusions may be drawn from the general results of the evaluation after exposure of the samples to accelerated aging:

- Samples without light stabilizers:
  . samples in accordance with the present invention: slight whitening (increase in lightness), slight variation in colour (ΔC*).
  . samples based on polyester resins: strong chromatic variation (ΔE* andΔC*), and in particular considerable yellowing, and considerable chromatic surface variability (yellowish marbling).
- Samples with light stabilizers (hydroxybenzophenones + HALS):
  . samples in accordance with the present invention: very slight whitening, insignificant variation in colour (ΔC*)
  . samples based on polyester resins: strong variation in colour (ΔE* andΔC*), in particular yellowing, chromatic surface disuniformity.

The mechanical resistance of the artificial marble and granite of the present invention is almost the same as those of similar products derived from polyester resins and 2 - 3 times higher than those of the corresponding natural material which contains the mineral filler in a grosser particle size. For example, the ultimate flexural stress of the present artificial marble and granite is 400 - 700 kg/cm^2, whereas that of the corresponding natural material is 150 - 250n kg/cm^2.

Compared with the artificial marble prepared by the already known process which uses a polymerizable poly(allyl carbonate), the artificial marble and granite of the present invention has a different kind of aesthetic effect and is much more economical, owing to the small quantities of polymerizable poly(allyl carbonate) required for its production. This possibility of using such low quantities of polymerizable poly-(allyl carbonate), in accordance with the present invention, is due to the use of a grosser (larger sized) filler, which shows a smaller wettable surface area, together with the excellent wetting characteristics of the polymerizable poly(allyl carbonates) used. It is, however, equally surprising that products with such extraordinary mechanical characteristics can be obtained with such low quantities of organic binder.

The invention will be further illustrated by the following examples.

In these examples, PRODUCTS A, B, C and D are used as polymerizable poly(allyl carbonates), with the following compositions and characteristics:

PRODUCT A:

Liquid product of the transesterification of di(allyl carbonate) and diethylene glycol (molar ratio 12/1). This product may be represented by formula (I) specified above, where R is the diethylene glycol radical and the monomer and the oligomers have the following distribution by weight: 88.3% (n = 1), 10.5% (n = 2), 1.1% (n = 3), 0.1% (n = 4). This product has a density of 1.15 g/ml at 20 °C and a viscosity of 14 cSt at 25 °C.

PRODUCT B

Liquid product composed of a mixture of:

- 37% by weight of PRODUCT A described above:
- 37% by weight of the product of the transesterification of di(allyl carbonate) and diethylene glycol (molar ratio 2/1), representable by formula (I) above, with the following distribution by weight of monomer and oligomers: 33.9% (n = 1), 25.1% (n = 2), 16.6% (n = 3), 10.2% (n = 4), 14.2% (n > 4);
- 26% by weight of tris(allyl carbonate) of tris(hydroxyethyl) isocyanurate, which is the transesterification product of di(allyl carbonate) and tris(hydroxyethyl)isocyanurate (molar ratio 12/1) and consists of 75% by weight of monomer and 25% by weight of oligomers. PRODUCT B has a density of 1.209 g/ml at 20 °C and a viscosity of 81 cSt at 25 °C.

PRODUCT C

Liquid product composed of a mixture of:

- 24% by weight of PRODUCT A described above;
- 24% by weight of th product of the transesterification of di(allyl carbonate) and diethylene glycol (molar ratio 2/1), with the same distribution of monomer and oligomers as described for PRODUCT B;
- 52% by weight of tris(allyl carbonate) of tris(hydroxyethyl)isocyanurate which is the transesterification product of di(allylcarbonate) and tris(hydroxyethyl)isocyanurate (molar ratio 12/1) and consists of 75% by weight of monomer and 25% by weight of oligomers. PRODUCT C has a viscosity of 320 cSt at 25°C.

PRODUCT D

Liquid product composed of a mixture of monomer and oligomers derived from the transesterification reaction of di(allyl carbonate) and a mixture of diethylene glycol and pentaerythritol in a weight ratio of 70/30, with a molar ratio of di(allyl carbonate) to the sum of the polyols of 5/1.

PRODUCT D has a density of 1.190 g/ml at 20°C and a viscosity of 90 cSt at 25°C.

PRODUCT E

Liquid product composed of a mixture of monomers and oligomers derived from the transesterification reaction of di(allyl carbonate) and a mixture of neopentyl glycol and tris(hydroxyethyl)isocyanurate in a weight ratio of 50/50, with a molar ratio of the di(allyl carbonate) to the sum of the polyols of 5/1.
Product E has a density of 1.184 g/ml at 20°C and a viscosity of 320 cSt at 25°C.

EXAMPLE 1

1,000 g of Serizzo Formazza granite, with the following particle size distribution:
60% by weight 1 - 4 mm,
20% by weight 0.1 - 1 mm,
20% by weight 5 - 100 µm (for more than 95%),
are mixed with a solution composed of 165.9 g of PRODUCT A and 10.6 g (6% by weight) of dicyclohexyl percarbonate, for 0.5 hours in a 2 litre polyethylene beaker, inclined and rotating at a low speed.

The mixture obtained is filled into a flat, open, steel mould (dimensions of 30 x 15 cm and height of 2 cm) protected with a thin sheet of high density polyethylene.

The mould is subjected fo 0.5 hours to vibration of medium frequency using a manual vibrator and subsequently, after having it placed on an ultra-sound plate, to high frequency vibrations for 0.5 hours. In this way, the heterogeneous mass becomes compact, continuous and damp and any interstitial air bubbles are eliminated.

The mould is then placed in an oven, under forced vacuum, for 0.5 hours and subsequently under a nitrogen atmosphere and is subjected to the following thermal cycle:
1.5 hours at 60°C,
1.5 hours at 70°C,
1 hour at 80°C.

The resulting panel, which is compact and perfectly hardened, is removed from the mould, calibrated on both sides to a thickness of 12 mm and the edges are trimmed with diamond-pointed tools, whereafter the panel is polished on one side with a brush based on silicon carbide. This side is shiny with a slight "orange-peel" effect, and resembles commercial Serizzo Formazza granite which is continuous, flat and polished.

EXAMPLE 2

Under the conditions described in example 1, 1,000 g of commercial Imperial Red granite from Sweden, with the following particle size distribution:
60% by weight 1 - 5 mm,
20% by weight 0.1 - 1 mm,
20% by weight 5 - 100 µm (for more than 95%),
are mixed with a solution of 167.7 g of PRODUCT B and 8.8 g (5% by weight) of dicyclohexyl percarbonate.

The resulting mixture is filled into a mould and subjected to vibration and polymerization, using the

same procedure as in example 1.

The resulting panel, which is compact and perfectly hardened, is calibrated to a thickness of 12 mm and polished on one side as in example 1. This side is shiny, with a slight "orange-peel" effect, and resembles the original Imperial Red granite from Sweden, which is continuous, flat and polished.

EXAMPLE 3

1,000 g of commercial Imperial Red granite from Sweden, crushed as in example 2, are mixed with 176.5 g of a mixture composed of 141.2 g (80% by weight) of PRODUCT B, 26.5 g (15% by weight) of vinyl versatate (VEOVA®-10 available from Shell) and 8.8 g (5% by weight) of dicyclohexyl percarbonate.

The mixture thus obtained is filled into a mould, subjected to vibration as described in example 1 and polymerized with the following thermal cycle:

1 hour at 60° C,
1 hour at 70° C,
1 hour at 80° C.

The resulting panel, which is compact and perfectly hardened, is calibrated to a thickness of 12 mm, smoothed and polished as described in example 1. The polished side resembles that of the panel of example 2.

EXAMPLE 4

6 kg of white Carrara marble, with the following particle size distribution:
65% by weight 0.5 - 1.5 mm,
15% by weight 100 - 500 µm,
20% by weight 5 - 100 µm (for more than 95%),
are mixed with a solution composed of 1,007 g of PRODUCT B and 53 g (5% by weight) of dicyclohexyl percarbonate for 0.5 hours in a 10 litre polyethylene container, inclined and rotating at low speed.

The mixture thus obtained is charged to a parallelepiped steel box, the base of which has a size of 20 x 15 cm and the internal walls whereof are treated with a silicone release agent. The box is subjected to medium and high frequency vibrations, operating under vacuum, and is then placed in an oven, first under vacuum and subsequently under a nitrogen atmosphere, as described in example 1. The following thermal cycle is used for the polymerization:

4 hours at 40° C,
4 hours at 50° C,
2 hours at 60° C,
2 hours at 70° C.

The resulting block (dimensions 10 x 15 x 20 cm) is removed by cutting the box. It is compact and perfectly hardened and is cut vertically into 1 cm thick slices. The surface of the cut is homogeneous: there are a few small bubbles. When this surface is smoothed and polished, it is white; the speckled and "orange-peel" effect is hardly noticeable.

EXAMPLE 5

A sheet (30 x 30 x 1.4 cm) is prepared by starting from a mixture of:
3,600 g of white Carrara marble, with the same particle size distribution as specified in example 4,
305 g of a solution composed of 286.7 g of PRODUCT D and 18.3 g (6% by weight) of dicyclohexyl percarbonate,
3 g of gamma-methacryloxypropyl-triethoxysilane.

In particular, the mixing is carried out in an open-air planetary mixer. The mixture is stirred for 10 minutes. The resulting mixture which is in the form of an uncaked, sandy mass which is slightly wet, is charged to a flat steel mould protected with polyethylene paper. The mould is subjected to a vacuum of 10 mm Hg, and then to violent vibro-compression for 1 minute. The resulting panel which is continuous, compact, plastic and self-consistent, is removed from the mould and, while still protected with the polyethylene paper, is polymeriz d between two aluminium plates heated by means of hot oil circulation, at 60° C for 8 hours.

The resulting panel which is perfectly hardened, is then calibrated to a thickness of 1.4 cm, trimmed, smoothed and polished as described in example 1. The polished side is white and shiny, with a slightly speckled and bar ly visible "orange-peel". The ultimate flexural strength of this material, determined with an

bis(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacate

. UVASIL® 299 (ENICHEM SYNTHESIS)

poly-methylpropyl-3-oxy-[4-(2,2,6,6-t tramethyl)-piperidinyl]-siloxane

. HALS-Acrylate

· 2,2,6,6-tetramethyl-4-piperidyl-acrylate

. CHIMASSORB® 90 (CIBA)

2-hydroxy-4-methoxy-benzophenone

. CHIMASSORB® 81 (CIBA)

2-hydroxy-4-acetoxy-benzophenone.

The samples were subjected to accelerated aging in the following two apparatus:

- ATLAS Ci 65 Weather-O-Meter;
  - . 6500 Watt Xenon lamp;
  - . Relative humidity 50%;
  - . Temperature of the black panel 60 °C;
  - . Exposure cycle: continuous irradiation;
  - . Exposure time: 2000 hours;
- UV-CON ATLAS
  - . FS 40 fluorescent lamp;
  - Exposure cycle: irradiation for 8 hours at 60 °C, and then darkness for 4 hours at 40 °C, with abundant condensed moisture on the surface of the samples;
  - . Exposure time: 1000 hours.

The evaluation was based on a measurement of the difference in colour of the samples from the beginning to the end of exposure; the evaluation parameters were taken from the tristimulus colorimetry, and in particular the following values were determined:

- ΔE^*: total variation in colour
- ΔC^*: variation in colour excluding the lightness parameter.

The quantitative results are shown in the table below.

As far as quality is concerned, the following conclusions can be drawn:

- Samples based on PRODUCT C and PRODUCT E:

  Those without stabilisers show a slight whitening and slight variation in colour (ΔC^*), samples 8 being better than samples 7.

  Samples with light stabilizers show a very slight whitening and insignificant variation in colour (ΔC^*). In general, however, the chromatic variations (ΔE^* andΔC^*) of samples based on PRODUCT E are of a lower degree than those based on PRODUCT C.
- Samples based on polyester resin (PES).

  Those without stabilizers undergo considerable chromatic variation (ΔE^* andΔC^*) and, in particular, show considerable yellowing and great chromatic surface variability (yellowish marbling).

  Samples with stabilizers show a significant variation in colour (ΔE^* and ΔC^*), and in particular yellowing and chromatic surface disuniformity.

  The overall appearance of all samples, however, is much poorer than that of the corresponding samples based on PRODUCTS C and E.

TABLE

Test sample/example	7	8	9	10	11	12	13	14	15	16	17[a]	18[a]
Binder	C	E	PES	C	PES	C	PES	E	PES	E	E	PES
Chimassorb® 90	/	/	/	0.5	0.5	0.5	0.5	/	/	0.5	0.5	0.5
Chimassorb® 81	/	/	/	/	/	/	/	0.5	0.5	/	/	/
Tinuvin® 292	/	/	/	/	/	0.5	0.5	/	/	/	/	/
Uvasil® 299	/	/	/	/	/	/	/	0.5	0.5	/	0.5	0.5
Hals - Acrylate	/	/	/	/	/	/	/	/	/	0.3	/	/
WOM 2000 hrs.: ΔE*	10	2.3	10.5	5	7	1.5	3.9	0.8	3.5	0.6	0.7	3.2
ΔC*	2.5	0.8	8.5	1	4.5	0.6	2.9	0.45	2.6	0.4	0.4	2.8
UV-CON 1000 hrs.: ΔE*	8	2.7	11[b]	5	7.5[b]	1.8	4.5[b]	0.9	3.8[b]	0.7	0.6	3.8[a]
ΔC*	3	0.9	8[b]	1.5	5[b]	0.7	3.4[b]	0.5	3.3[b]	0.3	0.35	2.7[a]

a: test samples are red as they contain 0.2% by weight of the pigment BAYFERROX® 140 M

b: the colour is highly heterogeneous

Claims

1. Composition for producing artificial marble or granite, containing (a) a liquid, polymerizable polyol-based poly(allyl carbonate) binder and (b) a mineral filler, wherein
   - the mineral filler (b) is of the carbonate type in th case of marble and of the silicate or silica type

in the case of granite, said carbonate, silicate or silica mineral filler being in the form of particles of which 40 to 100% by weight have a particle size of at least 0.5 mm;
- the polymerizable poly(allyl carbonate) (a) is present in amounts of from 4 to 30 parts by weight per 100 parts by weight of the total of poly(allyl carbonate) (a) and mineral filler (b).

2. Composition according to claim 1, wherein the mineral filler is selected from natural marble, granite and silica sand.

3. Composition according to any one of claims 1 and 2, wherein from 50 to 80% by weight of the mineral filler are composed of particles having a size of at least 0.5 mm, the remainder being composed of particles having a size of less than 0.5 mm, and preferably having a size ranging from 1 to 499 µm, said smaller particles being of the same or different origin as compared to the larger particles.

4. Composition according to claim 3, wherein the smaller particles are composed of or comprise hydrated alumina, talc, silica, graphite, mica or mixtures thereof.

5. Composition according to any one of claims 3 and 4, wherein the finer particles are partially replaced by long and/or short glass fibres.

6. Composition in accordance with any one of the preceding claims, wherein said mineral fillers, both fine and gross, are pre-treated with silane compatibilizing agents, particularly with gamma-methacryloxypropyl-triethoxy silane, vinyl triethoxysilane and/or trimethylsilane.

7. Composition according to any one of the preceding claims, wherein the polymerizable poly(allyl carbonate) (a) comprises at least one poly(allyl carbonate) of a polyol containing from 2 to 6 hydroxy groups in the molecule, in the form of a monomer and/or oligomer.

8. Composition according to claim 7, wherein component (a) is selected from:
(i) bis(allyl carbonates) of diols, particularly of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, pentanediol, hexanediol, di-(hydroxymethyl)cyclohexane, neopentyl glycol, and di(hydroxymethyl)tricyclodecane;
(ii) tris(allyl carbonates) of triols, particularly of glycerol, trimethylolpropane and tris(hydroxyethyl)-isocyanurate;
(iii)tetra(allyl carbonate) of pentaerythritol;
(iv) hexa(allyl carbonate) of dipentaerytrhitol;
(v) bis(allyl carbonate) of diethylene glycol monomer of general formula (I):

$$CH_2=CH-CH_2-O-\underset{\underset{O}{\|}}{C}-O-(R-O-\underset{\underset{O}{\|}}{C}-O)_n-CH_2-CH=CH_2 \qquad (I)$$

where R represents CH_2-CH_2-O-CH_2-CH_2 and n = 1;
(vi) mixtures of bis(allyl carbonate) of diethylene glycol monomer of general formula (I) wherein n = 1 with one or more oligomers of bis(allyl carbonate) of di-ethylene glycol of general formula (I) wherein n ranges from 2 to 10, the quantity of said monomer compound ranging from 20 to 90% by weight;
(vii)mixtures of
(1) bis(allyl carbonate) of diethylene glycol monomer;
(2) bis(allyl carbonate) of diethylene glycol oligomer; and
(3) tris(allyl carbonate) of tris(hydroxyethyl)isocyanurate; component (1) being present in quantities ranging from 10 to 50%, component (2) being present in quantities of from 20 to 70% and component (3) being present in quantities of from 5 to 60% by weight, component (3) being optionally in the form of an oligomer;
(viii) transesterification products of a mixture of diallyl carbonate, diethylene glycol and tris-(hydroxyethyl)isocyanurate;
(ix) mixtures of
(1') bis(allyl carbonate) of diethyl n glycol monomer;

(2') bis(allyl carbonate) of diethylene glycol oligomer; and

(3') tetra(allyl carbonate) of pentaerythritol; component (1') being present in quantities ranging from 10 to 50%, component (2') being present in quantities of from 20 to 70% and component (3') being present in quantities of from 5 to 60% by weight, component (3') optionally being partially in the form of an oligomer; and/or

(x) transesterification products of a mixture of diallyl carbonate, ethylene glycol and pentaerythritol.

9. Composition according to any one of the preceding claims, wherein the polymerizable poly(allyl carbonate) (a) is present in the composition in quantities of from 6 to 20, particularly 7 to 8 parts by weight per 100 parts by weight of the total of said poly(allyl carbonate) (a) and said mineral filler (b).

10. Composition according to any one of the preceding claims, wherein the polymerizable poly(allyl carbonate) (a) is substituted, up to a maximum of 40% by weight, by monofunctional vinyl and/or (meth)acrylic monomers, particularly vinyl acetate, vinyl versatate and/or methyl methacrylate.

11. Composition according to any one of the preceding claims, which is characterized by additionally containing a polymerization initiator for the poly(allyl carbonate) (a), said initiator being selected from peroxides and nitrocompounds, particularly from percarbonates such as dicyclohexyl peroxy-dicarbonate and diisopropyl peroxy-dicarbonate.

12. Composition according to claim 11, wherein the initiator is present in amounts of from 1 to 10% by weight, particularly from 3 to 7% by weight, with respect to the weight of the poly(allyl carbonate) (a).

13. Composition according to any one of the preceding claims, which additionally contains one or more of the following components: silanes, dispersers and/or wetting agents for the mineral fillers, deaerating agents, viscosity reducing agents, antisettling agents, internal release agents, preferably of the silicone type, titanium dioxide and organic and, preferably, inorganic dyes, organic and inorganic flame retardants, metallic dyes and/or lamellae, organic and inorganic pearly dyes and/or lamellae, stabilizers such as UV absorbers of the hydroxybenzophenone and benzotriazole type and/or UV stabilizers such as sterically hindered amines (HALS).

14. Process for the preparation of artificial marble and granite, comprising the steps of:

(a) preparation of a composition for producing artificial marble or granite according to any one of the preceding claims by mixing the corresponding components;

(b) pouring the resulting mixture into a mould and compacting it, optionally under vacuum to eliminate occluded air;

(c) thermal polymerization of the binder (a) to obtain a slab or block; and

(d) finishing the slab or block thus obtained.

15. Artificial marble or granite, obtainable from the composition according to any one of claims 1 to 13.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91122032.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP - A - 0 308 973 (ASAHI GLASS COMPANY LTD.) * Totality * --	1-15	C 04 B 26/18
D,X	JP - A - 61-111 953 (FUKUBI KAGAKU KOGYO KK.) * Totality * --	1-15	
D,X	US - A - 4 698 010 (TONCELLI) * Totality * --	14	
P,X	JP - A - 3-86 710 (NIPPON OILS & FATS CO. LTD.) * Totality * ----	1-15	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	02-03-1992	BECK

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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